SCIENCE FOR GLASS PRODUCTION

UDC 666.19.621

OBTAINING BASALTIC CONTINUOUS AND STAPLE FIBERS FROM ROCKS IN KRASNODAR KRAI

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Translated from *Steklo i Keramika*, No. 6, pp. 3 – 6, June, 2010.

The possibility of using rocks form the Khatsavitskoe, Solokhaul'skoe, and Tugupskoe deposits in Krasnodar Krai in the production of basaltic fibers has been investigated. Using laboratory single-spinneret setup it is shown that continuous, thickened, and rough fibers are formed from melts of these rocks in a wide temperature interval. Using a setup with an induction method of melting the raw materials and acoustic blowing of the melt with compressed air, commercial prototype batches of superthin staple fibers, whose main technical characteristics fall into the range regulated by GOST 4640–93, were obtained.

Key words: rocks, melt, glass, basaltic continuous and staple fibers, modulus of acidity, viscosity, surface tension, crystallizability, temperature interval of fiber drawing.

Fibers from rock melts perform at least as well as and in some respects better than mineral and glass fibers — application temperature, hygroscopicity, durability, resistance to gaseous and liquid corrosive media. Magmatic rocks are used as the initial single-component raw material for the production of basaltic fibers — gabbro, amphibolites, andesites, porphyrites, diabases, basalts, and others, the deposits of which on the territory of Russia total hundreds of billions of cubic meters, i.e. practically inexhaustible. The mineral-raw materials resources of Krasnodar Krai also include basaltoid rocks, whose investigation for the production of basaltic stable and continuous fibers, thermal insulation and construction materials based on them is of great interest for the comprehensive development of the local raw materials resources of industry.

Undoubtedly, each deposit has its own particulars, which must be taken into account when developing the technical processes for obtaining fibers and articles from them. This requires determining the chemical composition of the raw materials and evaluating the physical-chemical and technological properties of melts.

The materials for the present work consisted of samples of pyroxene porphyrite and diabases obtained in the regions of the explored deposits of Krasnordar Krai — Khavatskoe, Solokhaul'skoe, and Tugupskoe deposits.

The main prerequisite for obtaining high-quality fibers is to use raw materials with a definite and, preferably, constant chemical property, which is characterized by the acidity modulus M_a calculated from the ratio of the acidic and basic oxides in the mix or melt:

$$M_a = \frac{SiO_2 + Al_2O_3}{CaO + MgO},$$

where SiO_2, Al_2O_3, CaO, and MgO are the mass contents of the oxides, %.

The water-resistance index pH of fibers, which characterizes their durability, depends on the chemical composition of the mix. The pH decreases as the content of the acidic oxides SiO_2 and Al_2O_3 in the mix increases. Correspondingly, the higher the value of M_a of the rock, the more resistant to hydrolysis the fibers obtained from it are. However, an increase of the acidity in the mix makes it more difficult to melt the mix, increases the viscosity of the melt, and ultimately results in lower productivity of the melter or higher energy consumption on melting. In the production of staple fibers (mineral wool), a negative factor is an increase with increasing viscosity of the melt of the diameter of an elementary fiber and the content of the nonfibrous inclusions — "beads."

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TABLE 1. Composition of the Rocks Studied

Oxide	Content, wt.%		
	porphyrite (Khatsavitskoe deposit)	diabase (Solokhaul'skoe deposit)	diabase (Tugupskoe deposit)
SiO_2	48.4	45.8	49.6
TiO_2	1.0	1.9	1.0
Al_2O_3	15.3	13.7	16.4
$FeO + Fe_2O_3$	13.4	9.2	10.0
MnO	0.2	0.1	0.2
MgO	5.8	6.5	5.6
CaO	10.2	10.7	4.3
$Na_2O + K_2O$	2.2	3.9	6.9
P_2O_5	0.5	0.3	0.2
Calcination losses	3.1	7.5	5.0
M_a	4.0	3.5	6.7

The chemical composition of the rocks studied, determined by means of x-ray fluorescence using an SRM-25 multichannel x-ray spectrometer, and the calcination losses are presented in Table 1.

According to the published data [1, 2], rocks with acidity modulus greater than 1.2 are suitable for obtaining staple and continuous fiber. The optimal chemical composition is considered to one that gives an acidity modulus from 3 to 6. In porphyrite and Solokhaul'skoe diabase M_a does not exceed theses limits, and the high value of the acidity modulus in Tugupskoe diabase makes it possible to classify this rock as refractory, processing of which into fiber requires increasing the energy consumption or introducing into the mix additional components in order to attain the required viscosity of the melt, which, naturally, with make the product more expensive.

The main parameters of the melt which determine its suitability for obtaining fibers and the behavior during manufacture of the product are the gas-saturation, chemical uniformity, surface tension and its temperature dependence, proneness to crystallization and wetting of the material used for the spinneret feeders.

The capability of glass melts to form fibers is characterized is characterized by the ratio of the viscosity to the surface tension, and the stability of the process and its technological parameters depend mainly on the crystallizability, viscosity, and rate of solidification of the melt, chemical uniformity of the glass mass and its content of gases [3]. High crystallizability and high value and sharp temperature dependence of the crystallizability have a negative effect on the stability of the fiber formation process and lower the temperature interval of fiber production. High gas saturation of the glasses can cause secondary gas release when fibers are formed from then and, in consequence, cause breaks of fibers during the manufacture of continuous fibers. Chemical uniformity is one of the important technological properties of glass. The higher it is, the more stable the fiber formation process. Low chemical uniformity can be due to inadequate founding and poor homogeneity of the molten glass, breakdown of the thermal regime in the glass making furnace, and other reasons.

Directly heated electric furnaces giving temperatures up to 1500°C and laboratory vessels made from platinum-rhodium melt were used to study the physical-chemical properties of the melt. The temperature in the furnaces was measured with a platinum-rhodium thermocouple, whose indications were output to a Sh 711 multichannel measuring transducer.

To start the glass founding process, the temperature interval where the experimental rock was determined by the method described in [4]. For this, the rock sample on a platinum plate was placed in a furnace and the temperature at which melting starts, at which the rock is observed to stick to the plate, and the final temperature, at which the sample is completely melted and does not contain solid particles and gas inclusions were measured. The experiments showed that all samples pass into melt at temperature no higher than 1450°C, which corresponds to the fusibility requirements for raw materials to be used in the production of any kind of fiber [2]. However, quartz inclusions and gas bubbles were observed in almost all molten glasses, so that chemically uniform, homogeneous melts were obtained in an induction furnace at 2000°C.

The investigations of the manufactures glasses under a microscope confirmed that the system passes into a single-phase amorphous state with a small number of gas inclusions, which is in agreement with the results of measurements of the surface tension (Table 2), whose high value determines the prolonged gas release in the glass founding process.

TABLE 2. Surface Tension of Samples at Different Temperatures

Rock (deposit)	Surface tension, N/m, at temperature, °C					t_{ULC}, °C
	1250	1270	1300	1350	1400	
Porphyrite (Khavatskoe)	0.370	0.373	0.378	0.381	–	1290
Diabase (Solokhual'skoe)	0.367	0.370	0.373	0.379	–	1295
Diabase (Tugupskoe)	–	0.370	0.386	0.389	0.392	1345
Sodium-silicate glass	0.320	0.323	0.325	–	–	–

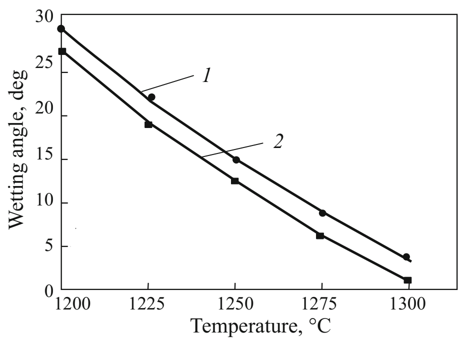

Fig. 1. Temperature dependence of the wetting angle melts on a plate made of platinum-rhodium alloy: *1*) prophyrite (Khatsavitskoe deposit), *2*) diabase (Solokhual'skoe deposit).

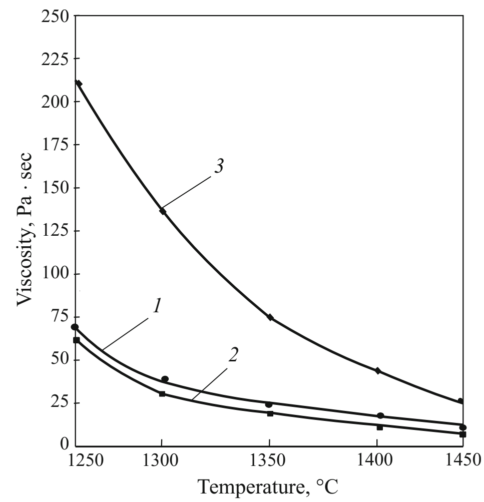

Fig. 2. Temperature dependence of the viscosity of melts of rocks: *1*) porphyrite (Khatsavitskoe deposit); *2*) diabase (Solokhaul'skoe deposit); *3*) diabase (Tugupskoe deposit).

Analysis of the results of determining the temperature of the upper limit of crystallization t_{ULC} of glasses (see Table 2) shows that the melts of porphyrite and Solokhaul'skoe diabase are less probe to crystallization, but their crystallizability is quite high, which sets a lower limit for the temperature interval of fiber production t_{IFP}.

An important factor determining the upper limit t_{IFP} is the flow of the molten glass along the spinneret plate, characterized by the wetting angle. The wettability of the platinum-rhodium melt from which commercial vessels and feeders are made, by iron-containing basaltic melts is much higher than that of sodium-silicate glasses and increases with temperature (Fig. 1), which, of course, affects the decrease of t_{IFP}.

On the basis of previously established criteria [5, 6] a viscosity from 3 to 9 Pa · sec is considered optimal for obtaining thin staple fibers by vertical blowing of melt by air. Such viscosity is attained in the melts studied, except for Solokhaul'skoe diabase, at temperatures above 1450°C. Continuous fibers are stably produced from melts whose viscosity is 5 – 15 Pa · sec at 1450°C and 20 – 100 Pa · sec at 1300°C. The viscosity of most rocks which are suitable for producing thin continuous fibers at the production temperature is 10 – 30 Pa · sec. The viscosity measured with a RVTs-L90R-4 viscosimeter fully satisfies these conditions only in the case of prophyrite (Fig. 2).

The proneness of melt to form continuous fiber was evaluated according to the temperature interval of fiber production on a single-spinneret laboratory setup, which includes an electric vertical furnace, a winding apparatus, and platinum crucibles with an opening in the bottom (spinneret) with diameter 1.8 mm for thin fiber and 3.6 mm for coarse fiber. The production of fiber is considered to be stable if there are no breaks in its production, no pulsation of the melt stream at the exit of the spinneret, and no nonuniformity of the filament along the diameter at a prescribed temperature.

It was impossible to draw a fiber through a 1.8 mm in diameter spinneret because of the high surface tension of the melts studied and the high crystallization and wetting powers: at 1350°C the molten glass, rising along the nose of the spinneret, spreads along the bottom of the crucible; as temperature decreases, the melt crystallized and does not spontaneously pass through the opening of the spinneret.

Thickened 14 – 28 μm in diameter fibers form from melts of Khatsavitskoe diabase and Solokhaul'skoe diabase with the sue of 3.6 mm in diameter spinneret and winding rate 1560 m/min in a wide temperature range (1320 – 1450°C). Coarse fibers (100 – 400 μm) were obtained, including from melt of Tugupskoe diabase, with speeds 5 – 6 m/min. It should be noted that the temperature interval of the production of coarse fibers for the last melt is narrower than for others because of the strong proneness to crystallization.

The thick and coarse fibers can be use for disperse reinforcement of concretes, asbestos-cement articles, gypsum tiles, and other articles.

Three batches of wool were obtained from the experimental rocks using the VM-10 apparatus, intended for obtaining mineral wool from superthin fiber by means of induction melting of rock in water-cooled crucible followed by blowing the melt with atmospheric air.

The production of wool from porphyrite and Solokhaul'skoe diabase was stable, and the product obtained satisfied all technical requirements of GOST-4660 for the VMST grade (Table 3). Wool could not be obtained from Tugupskoe diabase in the standard regime because of the high viscosity and rate of solidification. The refractory raw material required changing the regulations for the operating regimes of the melter in the direction of increasing the energy characteristics and raising the blowing pressure. In spite of this, high-viscosity glass solidified at the entrance into the blowing head; this was the reason for the presence of a larger number of coarse fibers and "beads", giving the fiber an elevated thermal conductivity, in the product obtained.

TABLE 3. Characteristics of Mineral Wool Obtained on the VM-10 Setup

Indicator	GOST 4640 requirements for VMST grade	Test results		
		prophyrite (Khatsavitskoe)	diabase (Solokhual'skoe)	diabase (Tugupskoe)
Density under specific load 98 Pa, kg/m^3	≤ 35	13.9	14.5	18.8
Moisture content, wt.%	≤ 1.0	0.18	0.14	0.12
Water resistance pH	≤ 4.0	2.1	2.2	2.1
Fiber diameter, μm	From 0.5 to 3.0	3.0	2.8	4.5
Mass fraction of nonfibrous inclusions larger than 0.25 mm, wt.%	≤ 5	4.74	4.39	4.96
Thermal conductivity at 25°C, W/(m · K)	≤ 0.041	0.040	0.039	0.045
Content of organic substances, wt.%	≤ 2.0	No	No	No

The experimental data obtained in laboratory and industry studies show that pyroxene porphyrite from the Khatsavitskoe deposit and diabase from the Solokhaul'skoe deposit can be worked into superthin (mineral wool), thickened and coarse fiber but are not recommended for thin continuous fiber. Diabase from the Tugupskoe deposit can be used to obtain mineral wool only after some calcium-containing is added to the diabase mix.

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